Crystal Chemistry and Structure-Property Relationships of Dielectric Ceramic Materials

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The preparation, modeled and refined crystal structures, and structure-dielectric property relationships of five $Ba_3MM'_2O_9$ (M = Mg, Ni, Zn; M′ = Nb, Ta) perovskites are reported. The 2:1 B-site cation ordered perovskites crystallize in the $P\bar{3}m1$ space group with ordered [111] planes of M and M′ cations. An algorithm was developed to calculate an ideal crystal structure by optimizing, within the symmetry constraints of the $P\bar{3}m1$ space group, the bond valence sums of each atom in the unit cell. Calculated crystal structures were used as initial structure models in the course of performing Rietveld refinements of the neutron powder diffraction data. Agreement obtained between the fractional coordinates of the calculated and refined crystal structures is indicative of the accuracy of the modeling approach. Bond valence sums calculated from the bond distances indicate Ba-O bonds are compressed and the M-O and M′-O_6 bonds are expanded from ideal lengths. A shift of Ta^{5+} and Nb^{5+} out of the center of the [M′O_6] octahedra results in the formation of three short and three long M′-O bonds. The octahedral distortion is driven by the asymmetry in the O bonding network and aided by the second-order Jahn-Teller distortion of the d^0 Nb^{5+} and Ta^{5+} cations. Differences in the atomic coordination environments in the crystal structures are utilized to propose crystal structure-dielectric property relationships. The coordination of the divalent B-site cation (M^{2+}) correlated with the temperature coefficient of the resonant frequency (τ_f); a more under-bonded M^{2+} exhibited a more negative τ_f. Also, the nearer the bond valences sums of the B-site cations were to the formal oxidations states, a higher $Q \times f$ was observed.

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